

Final Report for the DOE BES Program  
"The Science of Electrode Materials for Lithium Batteries"

1999-2007

For:

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## Introduction

Rechargeable lithium batteries continue to play the central role in power systems for portable electronics, and could play a role of increasing importance for hybrid transportation systems that use either hydrogen or fossil fuels. For example, fuel cells provide a steady supply of power, whereas batteries are superior when bursts of power are needed. The National Research Council recently concluded that for dismounted soldiers "Among all possible energy sources, hybrid systems provide the most versatile solutions for meeting the diverse needs of the Future Force Warrior. The key advantage of hybrid systems is their ability to provide power over varying levels of energy use, by combining two power sources." The relative capacities of batteries versus fuel cells in a hybrid power system will depend on the capabilities of both. In the longer term, improvements in the cost and safety of lithium batteries should lead to a substantial role for electrochemical energy storage subsystems as components in fuel cell or hybrid vehicles.

We have completed a basic research program for DOE BES on anode and cathode materials for lithium batteries, extending over 6 years with a 1 year phaseout period. The emphasis was on the thermodynamics and kinetics of the lithiation reaction, and how these pertain to basic electrochemical properties that we measure experimentally — voltage and capacity in particular. In the course of this work we also studied the kinetic processes of capacity fade after cycling, with unusual results for nanostructured Si and Ge materials, and the dynamics underlying electronic and ionic transport in  $\text{LiFePO}_4$ . This document is the final report for this work.

The results obtained under this program are described below in three sections:

1. Phase Stability and Phase Diagrams
2. Thermodynamics of Electrode Materials for Li Batteries
3. Dynamics of Transport in  $\text{LiFePO}_4$

The publication list follows below. Not all results from all publications are described in the following text. The description of the research is intended to cover highlights of the work that we consider representative of the archival publications in the list below.

## Publication List

### Ph.D. Theses

- Charles K. Witham, "The Effects of Alloy Chemistry on the Electrochemical and Hydriding Properties of Ni-Substituted  $\text{LaNi}_5$ ", Ph.D. in Materials Science, California Institute of Technology, June 4, 1999.  
presently: technical staff, JPL, deceased Aug. 2002.
- Adrian Hightower, "Lithium Electronic Environments in Rechargeable Battery Electrodes", Ph.D. in Materials Science, California Institute of Technology, July 14, 2000.  
presently: Assistant Professor of Physics, Occidental College.
- Yun Ye, "Interaction of Hydrogen with Novel Carbon Materials", Ph.D. in Materials Science, California Institute of Technology, August 8, 2000.  
presently: member of the Technical Staff, Siebel Systems
- Jason Graetz, "Electronic Environments and Electrochemical Properties of Lithium Storage Materials", Ph.D. in Materials Science, May 7, 2003.  
presently: Postdoctoral Fellow, Brookhaven National Lab.
- Yvan Reynier, "Electrode Thermodynamics and Kinetics for Lithium-Ion Batteries" (co-advised with Dr. Rachid Yazami, CNRS, Directeur de These). Ph.D. in Materials Science, Grenoble University, France. May 25, 2005.  
presently: Postdoctoral Fellow, CNRS, Grenoble.
- Yasunori Ozawa, "Aging Study of Positive Electrode Materials for Lithium Ion Batteries" (main adviser was Dr. Rachid Yazami, CNRS, Directeur de These). Ph.D. in Materials Science, Grenoble University, France. October 19, 2005.  
presently: Technical Staff, Enax Co., Japan.
- Joanna Dodd, "Phase Composition and Dynamical Studies of Lithium Iron Phosphate," thesis defense March 14, 2007.
- Shu Miao, "Electronic Structure of Energy Storage Materials" thesis defended Jan. 30, 2007.

### Publications in Archival Journals

- Y. Ye, C. C. Ahn, C. K. Witham, B. Fultz, J. Liu, A. Rinzler, D. Colbert, K. Smith and R. Smalley, "Hydrogen Adsorption and Cohesive Energy of Single-Walled Carbon Nanotubes", Appl. Phys. Lett., 74 (1999) p. 2307-2309.
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- R. Yazami, H. Gabrisch, and B. Fultz, "Self-organised carbon nanostrips with a new  $\text{LiC}_{10}$  structure derived from carbon nanotubes", J. Phys. Chem. B, **115** (2001) pp. 10585-10588.
- J. Graetz, A. Hightower, C. C. Ahn, R. Yazami, P. Rez and B. Fultz, "Electronic Structure of Chemically-Delithiated  $\text{LiCoO}_2$  Studied by Electron Energy Loss Spectrometry", J. Phys. Chem. B **106** (2002) pp. 1286-1289.
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- H. Gabrisch, R. Yazami, and B. Fultz "A Transmission Electron Microscopy Study of Cycled  $\text{LiCoO}_2$ ", J. Power Sources, **119** (2003) 674-679.
- Y. Reynier, R. Yazami, and B. Fultz "The Entropy and Enthalpy of Lithium Intercalation into Graphite", J. Power Sources, **119** (2003) 850-855.
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- J. Dodd, R. Yazami, and B. Fultz, "Phase Diagram of  $\text{Li}_x\text{FePO}_4$ ", Electrochem. Solid State Lett. 9 (2006) pp. A151-A155.
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## Publications in Conference Proceedings

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- C. K. Witham, A. Hightower, B. V. Ratnakumar, R. C. Bowman, Jr., and B. Fultz, "LaNi<sub>5-x</sub>M<sub>x</sub> Alloys in Rechargeable Batteries: Factors affecting Cycle Lifetimes", Proc. 14th Annual Battery Conference on Applications and Devices, Long Beach, CA, January, 1999, H. A. Frank and E. T. Seo, eds., (Inst. Electrical Electronic Eng., Piscataway, NJ) IEEE 99TH8371, p. 61-65.
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- H. Gabrisch, R. Yazami, and B. Fultz, "Electron Diffraction and X-Ray Studies of New LiC<sub>10</sub> and LiC<sub>8</sub> Structures in Chemically Lithiated Single Wall Carbon Nanotubes," Proceedings of the 200th Meeting of The Electrochemical Society, San Francisco, Oct., 2001.
- J. Graetz, A. Hightower, C. C. Ahn, R. Yazami, P. Rez, and B. Fultz, "Electron Energy-Loss Spectrometry and Mapping of Oxygen in Delithiated LiCoO<sub>2</sub>", Proceedings of the 200th Meeting of The Electrochemical Society, San Francisco, Oct., 2001.
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- Yvan Reynier, Brent Fultz and Rachid Yazami, "Thermodynamics and kinetics of self-discharge in graphite-lithium electrodes" Proc. 17th Annual Battery Conference on Applications and Devices, Long Beach, CA, January, 2002, E. T. Seo, ed., (Inst. Electrical Electronic Eng., Piscataway, NJ). IEEE 02TH8576 p. 145.
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- H. Gabrisch, R. Yazami and B. Fultz, "In-Situ TEM Studies of Crystal Structure Transformations in  $\text{Li}_{1-x}\text{CoO}_2$  at Elevated Temperatures", Proceedings of the 204th Meeting of The Electrochemical Society, Orlando, Florida, Sept, 2003.
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## Patents

- Ratnakumar V. Bugga, Brent Fultz, Robert C. Bowman, Jr., Subbarao Surampudi, Charles Witham, and Adrian Hightower, " $\text{LaNi}_5$ -Based Metal Hydride Electrode in Ni-MH Rechargeable Cells" U.S. Patent No. 5,888,665 issued March 30, 1999.
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A. Dailly, C. C. Ahn, R. Yazami and B. Fultz, “Methods for Purifying Carbon Materials”, patent application filed on March 16, 2005.

Y. Reynier, R. Yazami and B. Fultz, “Electrochemical Thermodynamic Measurement System”, patent application filed on August 3, 2006.

## Invited Talks

Our work on basic materials science issues has been well-received. Invited talks by Brent Fultz include presentations were at the TMS Annual Meeting, Seattle, WA, Feb. 2002, 11<sup>th</sup> International Meeting on Lithium Batteries, Monterey, CA June, 2002, International Battery Association in conjunction with the 5<sup>th</sup> Hawaii Battery Conference, Jan. 2003. LIBD 2003, Lithium Battery Discussion: Electrode Materials, Bordeaux - Arcachon, France, September 16, 2003, TMS Annual Meeting, Charlotte, North Carolina March 15-18, 2004, MIT Mechanical Engineering Department Seminar, Nov. 5, 2004, The Electrochemical Society Fall Meeting, Los Angeles, October 2005. Keynote talk at MIT Energy Nanotechnology International Conference, June, 2006. The Electrochemical Society Fall Meeting, Cancun, Mexico, October 2006.



# 1. Phase Stability and Phase Diagrams

## 1.1 Nano-Silicon and Nano-Germanium Anode Materials

There is international excitement in nanostructured materials, which will enable important technologies in the long term [1]. Advantages of nanostructured materials for anodes and cathodes include faster kinetics of lithium transport, minimized stress gradients in the materials, and a possible contribution of grain boundary regions to the capacity for lithium storage [2-9], but numerous other suggestions have been made and hundreds of studies have been reported. We recently tested several types of nanostructured anode materials for their electrochemical performance in Li coin cells. These include 100 nm thin films prepared by vacuum evaporation, and films of 10 nm nanocrystallites prepared by ballistic consolidation. We have tested half cells with nanostructured Cu, Ag, Au, Si, Ge, Sn, Pb, In, Zn, Sb, Bi, Co and Mn [10]. A spectacular capacity of 2,200 mAh/g with modest cycle life was achieved in half cells with nanostructured Si electrodes [11,12]. There was significant irreversible capacity on the first cycle, however, owing to the tendency of Si to form a passivating oxide layer. The element Ge has weaker oxidation tendencies, and has better first-cycle performance. Figure 3 shows that the cycle life of thin films of Ge is excellent, and the specific capacity is 1,700 mAh/g [13] (consistent with the composition  $\text{Li}_{4.4}\text{Ge}$ ). Useful rate capabilities to 1000C were achieved, suggesting these electrochemical cells could be used for services traditionally performed by capacitors. These materials may have a near-term application in solid-state microbatteries. Solid-state batteries have a problem with over-discharge, when the Li layer is lost and does not reform upon further charging. A Ge, Si, or even Au layer could serve as a memory of the location of the anode. A patent is being pursued for some of these developments.

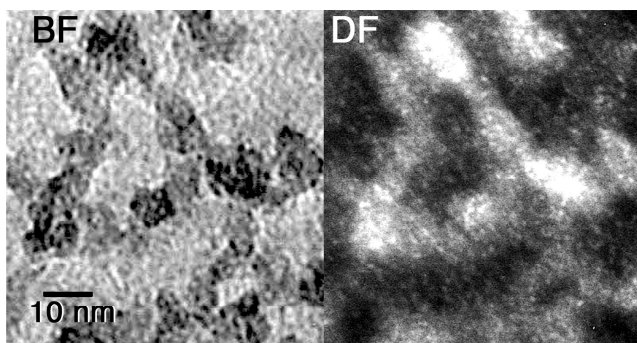


Fig. 3. (a) Bright- and dark-field TEM images of nanostructured silicon. The particles are connected in loose chains, but have widths < 10 nm.

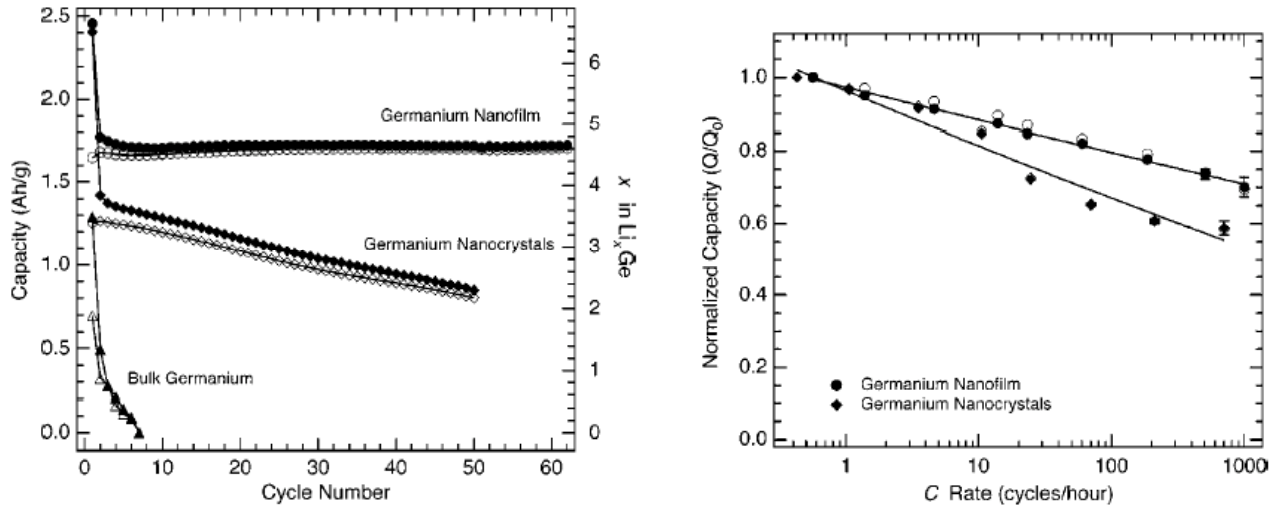


Fig. 3. (a) Left: Electrochemical capacity versus cycle number for evaporated thin films (100 nm) of Ge, dense Ge nanoparticles, and bulk Ge [13]. (b) Right: Rate capabilities of the evaporated Ge nanofilms and Ge nanoparticles [13].

## 1.2 Defects and Phase Changes in Anode and Cathode Materials

### 1.2.1 Partial Dislocations in $\text{LiCoO}_2$

The typical cathode in a rechargeable Li battery is based on the layered structure of  $\text{LiCoO}_2$ , comprising stacks of O-Co-O layers with planes of Li atoms between them. The typical “O3” phase of  $\text{LiCoO}_2$  allows for the removal of about half the Li atoms, but with further delithiations the structure becomes unstable. It transforms into “H1-3” and “O1” structures, which differ from the O3 structure by their sequence of stackings of O-Co-O layers [14-20]. These phases, and also the cubic spinel phase of  $\text{Li}_x\text{Co}_2\text{O}_4$ , have been associated with the cyclic degradation of the cathode after high voltage charging, but the degradation process is not well understood.

In work on  $\text{LiCoO}_2$  by transmission electron microscopy (TEM), we studied dislocations in the O3 structure, which had been observed previously [21,22]. By performing systematic tilting of the sample to orient the dislocations into null contrast conditions, we identified the Burger’s vector of the perfect dislocations. More interestingly, we discovered a splitting of these perfect dislocations into partial dislocations. Again using diffraction contrast analyses as in Fig. 1, these partial dislocations were found to have exactly the Burger’s vector necessary to transform the O3 structure into the H1-3 and O1 structures. Phase transformations by dislocations occur efficiently at low temperatures. Glide of these partial dislocations could be the mechanism that transforms layered  $\text{LiCoO}_2$  into the H1-3 and O1 structures upon delithiation. On the other hand, these partial dislocations cannot transform the O3 structure into the O2 structure [23,24], or into the cubic spinel form of  $\text{LiCoO}_2$  [25].

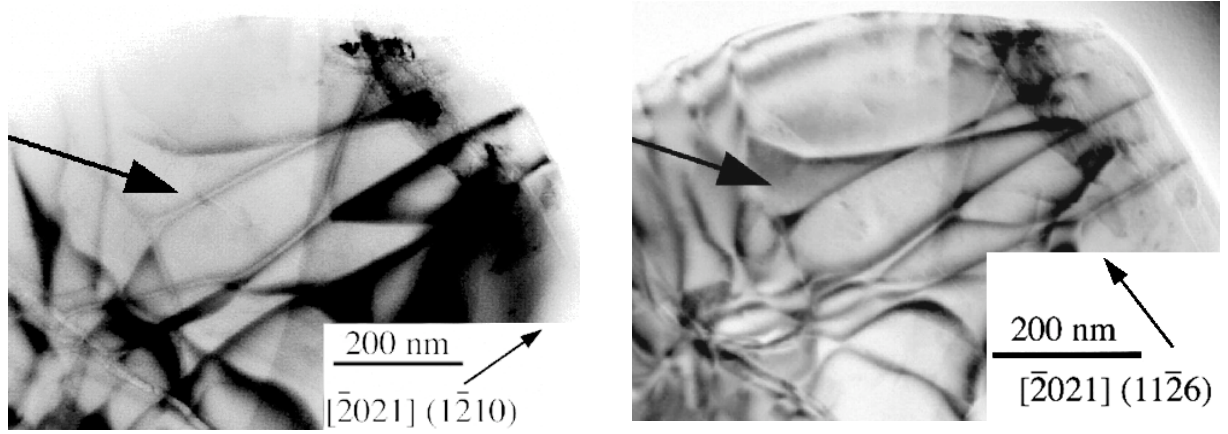


Fig 1. Typical invisibility conditions for two closely-split partial dislocations in  $\text{LiCoO}_2$ . (a) Two-beam image with  $k_0 = [2021]$   $\bar{g} = (1\bar{2}10)$ , showing that both partial dislocation lines are visible. (b) Image with  $k_0 = [2021]$  and  $\bar{g} = (11\bar{2}6)$ . The partial dislocation with Burgers vector  $a/3[0\bar{1}10]$  is visible, while the partial dislocation with  $b = a/3[1\bar{1}00]$  is now extinct [25].

### 1.2.2 Spinel Phase Formation in $\text{LiCoO}_2$

The spinel phase is known to be less active electrochemically compared to the layered O3 phase of  $\text{LiCoO}_2$ . The transformation to spinel phase seems to be irreversible, and could account for some capacity fade of the cathode upon cycling. In  $\text{LiCoO}_2$  subjected to hundreds of charge-discharge cycles, especially at temperatures of 70°C or so, we found some cubic spinel phase in the material by TEM study. This cubic spinel phase is well-known to be present in fresh  $\text{LiCoO}_2$  processed at lower temperatures [16,26], and had been reported previously in battery electrode material [21,22]. In our recent work, we identified cubic spinel phase formation on the surface of  $\text{LiCoO}_2$  particles that had the O3 structure before cycling. It appears that the cubic spinel layer grows thicker with further cycling at elevated temperatures. This could be a source of capacity fade, although a more quantitative correlation would be appropriate. As mentioned in section 1.1.1, it is not possible for this cubic spinel phase to form by a shear transformation of O3  $\text{LiCoO}_2$ . The spinel phase probably forms by nucleating on the surface of O3 particles, perhaps after dissolution of Co atoms during charging cycles. We found that the crystallographic orientation relationship between the O3  $\text{LiCoO}_2$  and the spinel phase is a precise one, as shown in Fig. 2 by the symmetric matching of two overlaying diffraction patterns.

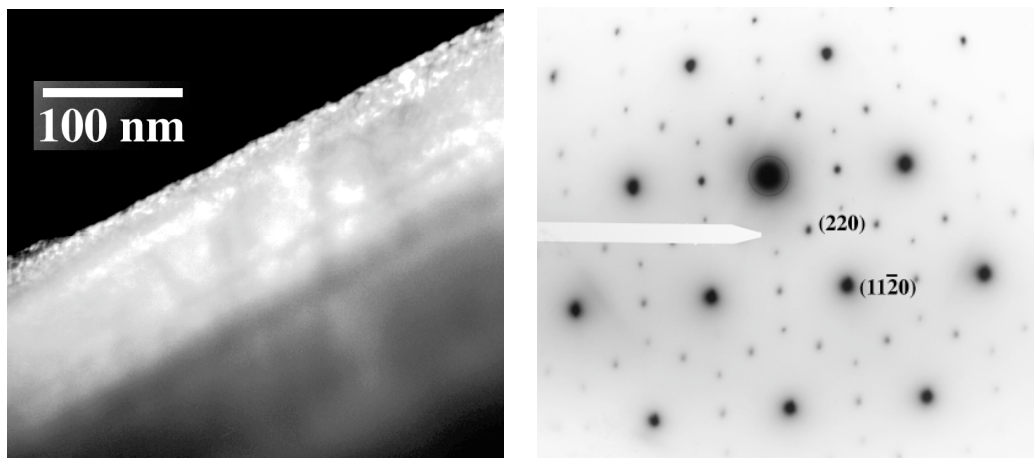


Fig. 2. (a) Layer of cubic spinel phase, approximately 100 nm thick, formed on the surface of a particle of O3 LiCoO<sub>2</sub>. Spinel phase (at top) has fine granular structure, O3 phase is smooth. (dark field image) (b) Selected area diffraction pattern from the surface layer of spinel phase and the O3 particle interior, showing overlain diffraction patterns consistent with the crystallographic orientation relationship: [0001] parallel to [111], and (11-20) parallel to (440).

### 1.2.3 Li in SWNTs

We found new phases in lithiated single-walled carbon nanotubes (SWNTs). Purified SWNT material was reacted with molten lithium at 220°C for two weeks, producing a material with the gold color characteristic of stage-1 Li-intercalated graphite. The x-ray diffraction (XRD) pattern was consistent with a monoclinic unit cell with an in-plane  $\sqrt{7}\times\sqrt{3}$  atomic arrangement corresponding to the composition LiC<sub>10</sub> [27]. The c-axis parameter was found close to 3.9 Å, 5% larger than in graphite LiC<sub>6</sub>. The TEM observations showed a multi-phase material that included both LiC<sub>10</sub> and some LiC<sub>8</sub>. Evidently a significant fraction of the SWNT material becomes graphene-like strips after exposure to molten lithium at 220°C for two weeks. Lithium is then intercalated between the carbon nano-strips, forming structures of LiC<sub>10</sub> and LiC<sub>8</sub> that had not previously been observed. The electrochemical cycling of these processed SWNTs showed a large initial irreversible capacity, however. The reversible capacity did not exceed 250 mAh/g.

### 1.2.4 Study of Self-Discharge of LiCoO<sub>2</sub> Cathode Materials

After a charged cell is aged at an elevated temperature, some loss of capacity is typically observed. Most of this loss is usually "reversible", and is recovered after recharging. In our study of the thermal aging of charged cells, changes in x-ray lattice parameters were used to monitor the Li concentrations in Li<sub>x</sub>CoO<sub>2</sub> after the aging treatments caused capacity losses. We found that a major part of the reversible capacity loss came from lithium re-intercalation into Li<sub>x</sub>CoO<sub>2</sub> when it was aged in the presence of a Li salt (LiClO<sub>4</sub>) in different media. This requires some electrolyte decomposition, and reintercalation rates depended on the solvent. On the other hand, thermal aging at 75°C in the presence of pure PC or pure argon gas resulted in other changes such as the formation of spinel phase. The spinel formation could account for some of the irreversible capacity loss in Li<sub>x</sub>CoO<sub>2</sub> cathodes after thermal aging [28].

### 1.3 Phase Diagram of $\text{LiFePO}_4$

$\text{LiFePO}_4$  has generated strong international interest as a promising cathode material for rechargeable Li batteries [29]. Recently the group in Amiens, France has found that at modest temperatures above room temperature, the heterosite ( $\text{FePO}_4$ ) and triphylite ( $\text{LiFePO}_4$ ) phases are no longer distinct [30,31]. At elevated temperatures, a new phase forms with the same  $\text{FePO}_4$  crystal framework, but with a unit cell that is intermediate to that of heterosite and triphylite. Subsequent work by our group has developed the phase diagram for  $\text{LiFePO}_4$  shown in Fig. 1. There is uncertainty in the phase boundary owing to sluggish kinetics at these low temperatures, but the unmixing transition is indeed reversible. This phase transition points\* a new path to alter the electrochemical performance of  $\text{LiFePO}_4$ , as discussed in Section 3.1.

The phase diagram for  $\text{Li}_x\text{FePO}_4$  has been determined for different lithium concentrations and temperatures. The two low temperature phases, heterosite and triphylite, have previously been shown to transform to a disordered solid solution at elevated temperatures. This disordered phase allows for a continuous transition between the heterosite and triphylite phases and is stable at relatively low temperatures. At intermediate temperatures the proposed phase diagram resembles a eutectoid system, with eutectoid point at around  $x = 0.6$  and  $200^\circ\text{C}$ . Kinetics of mixing and unmixing transformations are reported, including the hysteresis between heating and cooling. The enthalpy of this transition is at least  $700 \text{ J/mol}$ .

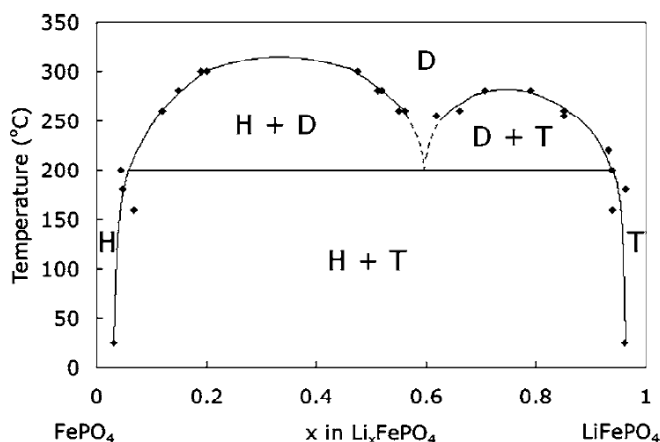


Figure 1. Phase Diagram of  $\text{LiFePO}_4$ , determined from x-ray diffractometry on samples quenched to room temperature [32]. The upper diamonds are temperatures for full disordering of the two-phase starting materials upon heating, the lower squares are temperatures for full unmixing of the quenched, disordered phase. For reasons of kinetics, we believe the actual phase boundary to be closer to the lower points.

\* We find no evidence of special structures at compositions  $x=0.5$  and  $x=0.75$  as reported by Delacourt, et al. [41], and they have no evidence that the new materials at these compositions are anything other than disordered phases [42].

## 2 Thermodynamics of Electrode Materials for Li Batteries

The large 4 V open circuit voltage of rechargeable Li batteries is a measure of the difference in chemical potential of Li atoms or ions in the anode and in the cathode. At room temperature, most of the contribution to the chemical potential is from the change in internal energy,  $E$ , of the Li atoms. A detailed picture of these changes can be obtained from electron energy-loss spectrometry measurements, especially in conjunction with modern electronic structure calculations. The large change in  $E$  originates with changes in the electronic environment of the Li atoms. The entropic contribution is much smaller —  $T\Delta S$  is of order 0.1 eV/atom. We studied both the energy  $E$  and the entropy  $S$  in well-ordered materials. In Sections 3.3 and 3.4 we propose to extend this work to more typical electrode materials.

### 2.1 EELS and Li Valence in Graphite

Electron energy loss spectrometry (EELS) is a sensitive probe of atomic valence, and how it changes at and around Li atoms in anode and cathode materials. One of our first efforts under this DOE BES program was the comparison of the Li  $K$ -edges in Li metal and in graphite near the composition  $\text{LiC}_6$  [33]. The experimental challenge was working with reactive samples in a TEM, especially the evaporated films of Li metal. Nevertheless, we did master the problems of oxidation and beam damage to obtain the result of Fig. 6. It shows clearly that Li atoms are neutral atoms when intercalated into graphite. The name “Li-ion” battery is therefore a misnomer. Although published in the year 2000 [33], this result produces strong reactions whenever it is presented at any meeting on lithium batteries.

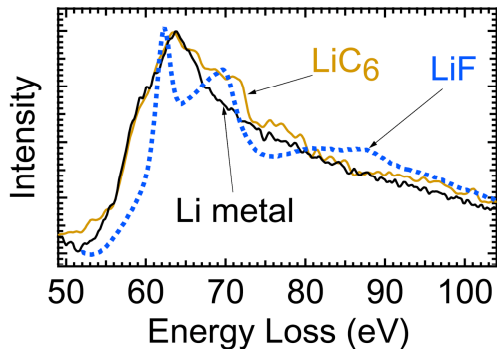


Fig. 6. Li  $K$ -edges in Li metal,  $\text{LiC}_6$ , and  $\text{LiF}$ , showing the similarity of edge onsets in Li metal and  $\text{LiC}_6$ .

### 2.2 Valence Changes with Lithiation in $\text{LiCoO}_2$

Electron energy-loss spectrometry (EELS) was used to measure the absorption edges of the elements in cathode materials. At the oxygen  $K$ -edges, a distinct pre-peak is found at 530 eV [34]. This pre-peak corresponds to electronic excitations from  $1s$  states to unoccupied  $2p$  states at the oxygen atoms. These  $2p$  states are hybridized with Co  $3d$  states, but the EELS spectra of the O  $K$ -edge measure the O  $2p$  component of this hybrid. It can be regarded as the part of the antibonding state situated at an oxygen atom. The dependence of the pre-peak intensity on Li concentration is presented in Fig. 4, showing that these O  $2p$  states are filled as Li is added to both  $\text{Li}_x\text{CoO}_2$  and  $\text{Li}_x(\text{Ni},\text{Co})\text{O}_2$ . Figure 4 also shows our calculations with the VASP code (per-



formed by Peter Rez), using input atom positions for partially-lithiated samples kindly provided by Van der Ven and Ceder [35]. Note the excellent agreement of the calculated (\*) and measured (•) results. The data are presented without any scaling parameters. The electron density provided by the VASP code shows that charge compensation for the Li electron occurs primarily at oxygen atoms. This is the qualitative interpretation of the data themselves, and the VASP predictions are in quantitative agreement with our experimental measurements. Such calculations have not yet been performed on  $\text{Li}_x(\text{Ni},\text{Co})\text{O}_2$ , but the experimental trend of Fig. 1 shows the same behavior — charge compensation of the Li electron occurs at O atoms rather than the Ni or Co atoms. This is consistent with recent theoretical work [36-38]. Not all experimental work has been interpreted in this way [39-43], but measurements of the O  $K$ -edge do show such behavior [34,44-47]. From measurements of the Ni and Co  $L_{2,3}$  edges, we found that there may be a small change in  $3d$  occupancy at Ni atoms, but not at Co atoms in our samples of  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  [34].

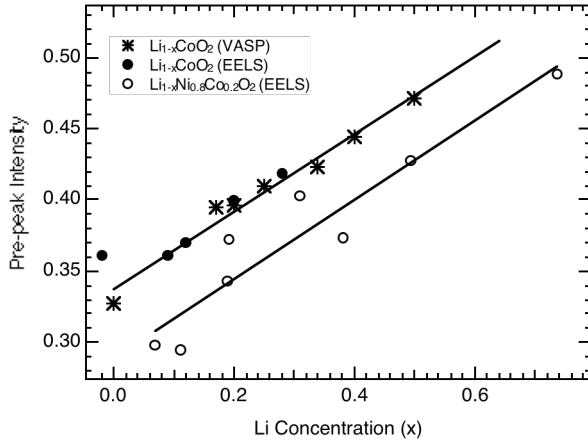


Fig. 4. Intensity of the O pre-peak versus Li concentration; VASP calculations and EELS measurements. In this figure,  $x$  denotes the loss of lithium, i.e., it corresponds to a composition  $\text{Li}_{1-x}\text{CoO}_2$ . Solid lines are best fits through the data [34,44].

### 2.3 Valence of Ni in $\text{Li}(\text{Ni},\text{Mn},\text{Co})\text{O}_2$

There is a large body of literature on the cathode materials  $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$  and  $\text{Li}_x\text{Ni}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$  stating that the removal of  $\text{Li}^+$  is compensated by the redox reaction of  $\text{Ni}^{2+}$  to  $\text{Ni}^{4+}$  [48-56]. We doubt this explanation, which is fundamentally different from the electronic structure changes in  $\text{Li}_x\text{CoO}_2$  as determined by ourselves and others [37,57-62], and from  $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$  as determined by our group [43,63-65]. Recently, samples of  $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$  and  $\text{Li}_x\text{Ni}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$  were prepared as active materials in electrochemical half cells. We cycled them electrochemically, and obtained different Li concentrations,  $x$ . Electronic absorption edges of Ni, Mn, Co, Li and O in these materials with differing Li content were measured by electron energy loss spectrometry (EELS) in a transmission electron microscope to determine the changes in local electronic structure caused by delithiation. The experimental absorption edges were generally consistent with work by others [52,53,66,67], showing a small shift in the Ni  $L_{2,3}$  edge with delithiation, but our more detailed analysis shows a different and more plausible interpretation than the formation of  $\text{Ni}^{4+}$ .

Our experimental work was supported by electronic structure calculations with the VASP pseudopotential package, the full-potential linear augmented plane wave code WIEN2K, and atomic multiplet calculations that took account of the electronic effects from local octahedral symmetry that were calculated by VASP and WIEN2K. The atomic multiplet calculations, performed by Peter Rez at Arizona State University, were crucial. The 2p-3d exchange inter-

action is strong for mid-3d transition metals, and affects the shape of the absorption edge [68]. These multiplet calculations showed that a valence change from  $\text{Ni}^{2+}$  to  $\text{Ni}^{4+}$  with delithiation would have caused a 4 eV shift in energy of the intense white line at the Ni  $L_3$  edge, but the measured shift was less than 1 eV. Additional evidence against the formation of  $\text{Ni}^{4+}$  (and  $\text{Ni}^{3+}$  to some extent) is found in the integrated areas of the  $L_{2,3}$  white lines shown in Fig. 2(a) and (b). The peak areas undergo changes that are too small to be explained as a change of valence at  $\text{Ni}^{2+}$  ions. Both EELS and the computational efforts showed that most of the charge compensation for  $\text{Li}^+$  takes place at hybridized O 2p-states, not at Ni atoms. A large change was found at the oxygen K-edge during delithiation, as shown in Fig. 2(d), and there are more O atoms than Ni atoms to compensate the charge.

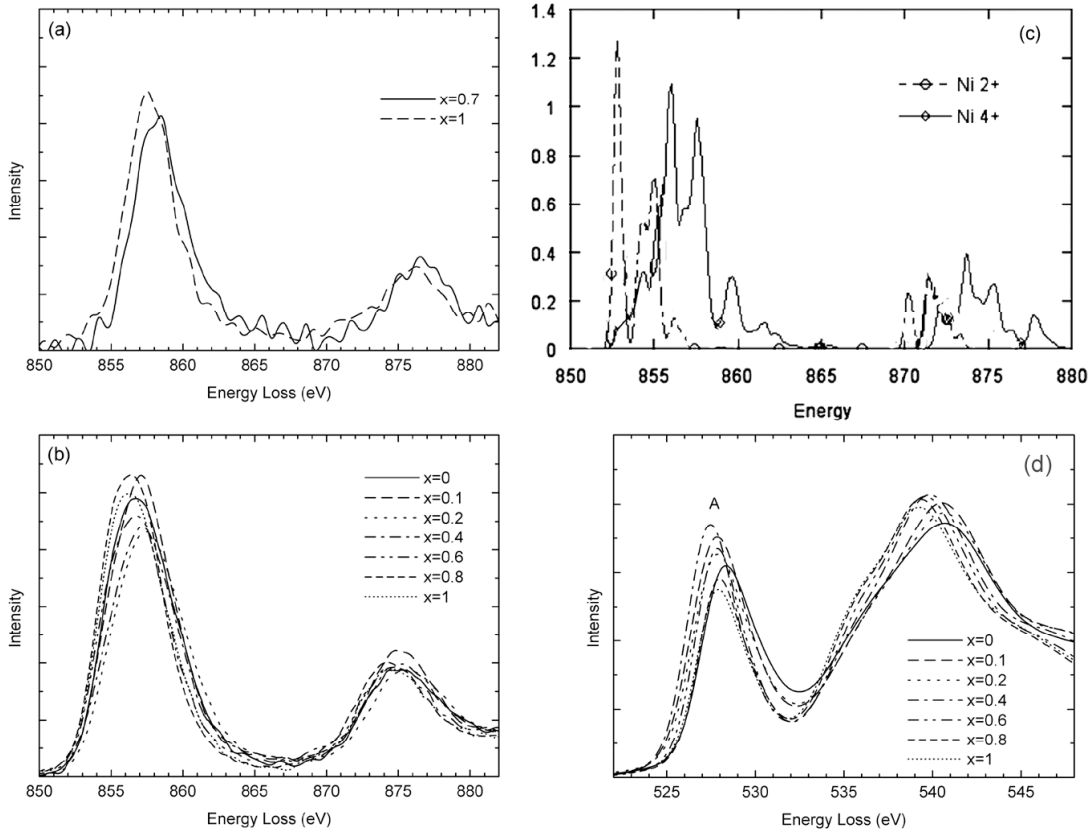


Figure 2. Ni  $L_{2,3}$  "white line" peaks from (a)  $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$  and (b)  $\text{Li}_x\text{Ni}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$  with different  $x$  values. (c) Atomic multiplet calculation of Ni  $L_{2,3}$  white lines, using crystal field information from WIEN2K. Compared to  $\text{Ni}^{2+}$ , the shift of the average  $L_3$  white line is 4 eV for  $\text{Ni}^{4+}$ , clearly inconsistent with the experimental results of parts a and b [69,70]. (d) Changes at the oxygen K-edge at  $\text{Li}_x\text{Ni}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$  during lithiation.



## 2.4 Entropy and Enthalpy of Lithium Intercalation into Graphite

Measurements of open-circuit voltages in half cells with graphite electrodes were used to obtain the entropy and enthalpy of lithium intercalation into carbon materials. Instrumentation was developed for automated measurements of open circuit voltages at different temperatures and states of charge. The method obtains the entropy and enthalpy of the lithiation reaction. natural graphite [71], and into meso carbon microbeads and cokes that were graphitized at various temperatures [72]. Some results are presented in Figure 4. For well-graphitized carbons shown in (b) and (d), at low lithium concentrations the entropy includes a large positive component identified as a configurational entropy of mixing. This corresponds to a relatively flat curve for the enthalpy of lithiation at small  $x$ , shown as an insert into (d). The entropy of intercalation changes sign at higher lithium concentrations, suggesting a second component. Raman spectroscopy and prior work on inelastic neutron scattering [73-78] indicate that this additional entropy is vibrational in origin. The situation is different for the more disordered carbons such as MCMBs heat treated at the low temperatures of 750°C and 1000°C. Here there is a broad spectrum of energies for Li sites as indicated by the steep slope of the enthalpy curve in Fig. 4(c), so there are relatively few insertion sites at a particular value of  $x$ . This suppresses the entropy of mixing at small  $x$ , as shown in Fig. 4(a).

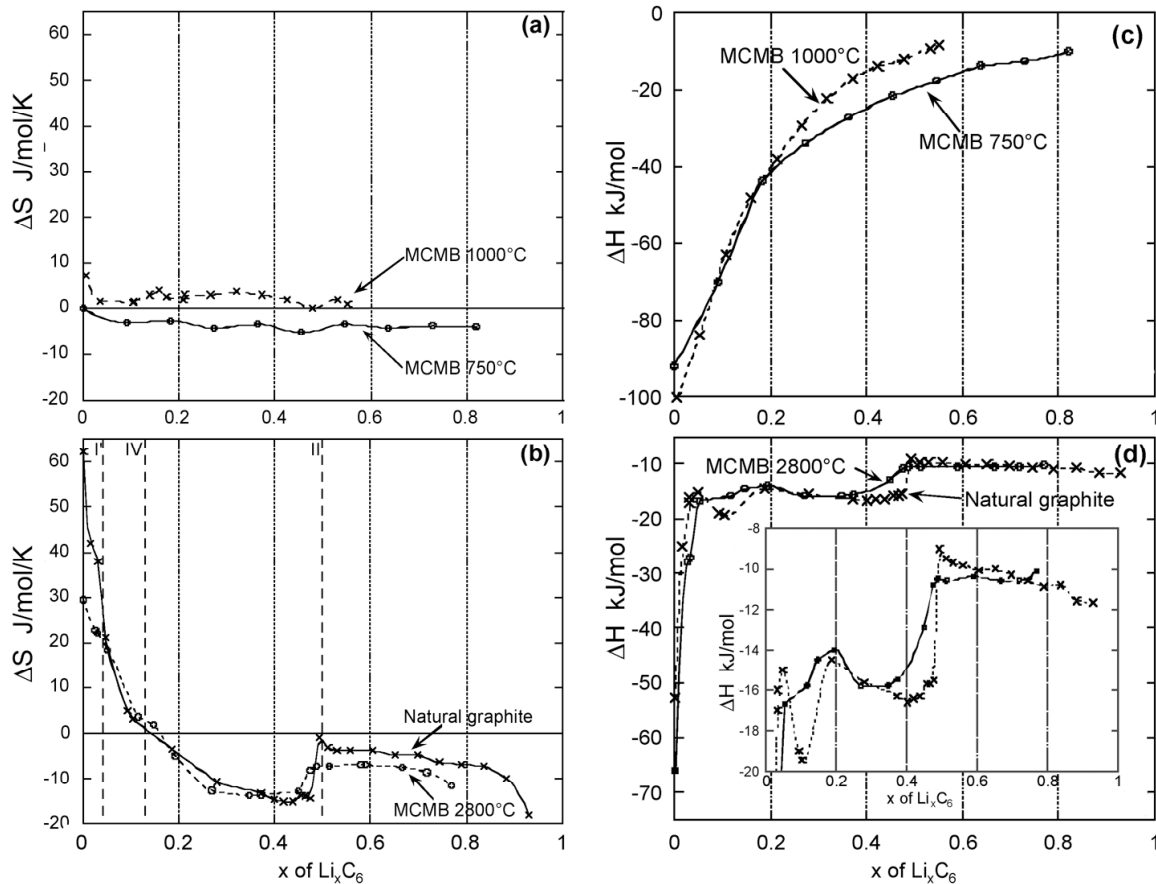


Figure 4. (a) Evolution of  $\Delta S$  versus Li concentration for MCMB heat-treated at 750 and 1000°C (b) same for MCMB heat treated at 2800°C and natural graphite (c) Evolution of  $\Delta H$  versus Li concentration for MCMB heat-treated at 750 and 1000°C (d) same for MCMB heat treated at 2800°C and natural graphite (insert is enlargement of same data).

## 2.5 Evolution of lithiation thermodynamics with the graphitization of carbons

An extensive study was performed on a series of cokes that were heat-treated at different temperatures to produce different degrees of graphitization. The thermodynamics of lithium intercalation in these materials were then measured. X-ray diffractometry and Raman spectroscopy were used to determine the structure of the carbon materials after heat treatment. The effect of the degree of graphitization on the entropy and enthalpy of lithium intercalation was thereby determined. A model is proposed to correlate the degree of graphitization to entropy profiles. It is shown that graphs of entropy versus open circuit voltage for different states of charge give quantitative information on graphitization, making them useful for the structural characterization of partially-graphitized carbons. Even if the physical origin of the parametric plots shown in Figure 6 are not fully understood, the shapes of these plots have a high sensitivity to structural changes in the graphite. A patent is being pursued for this type of materials characterization because it may see use in many other materials besides carbons.

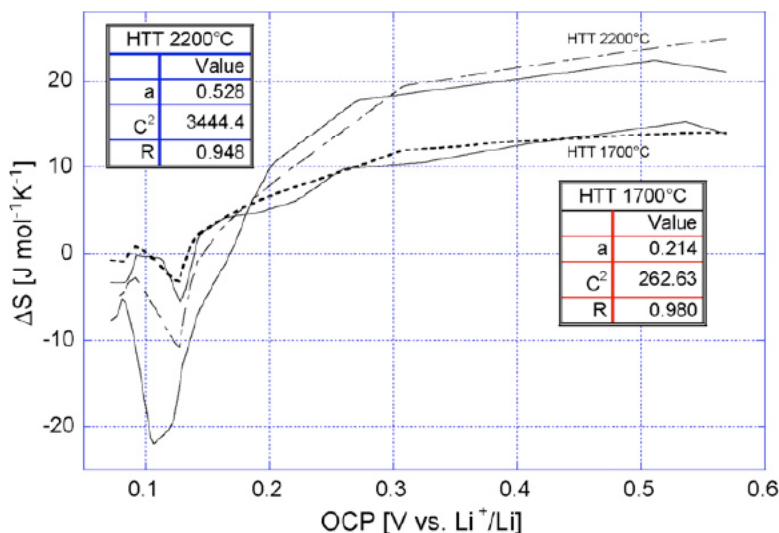


Figure 6. Parametric plots of entropy curve vs. OCV curve for two samples, heat-treated at 1700 and 2200 °C.

## 2.6 Entropy and Enthalpy of Lithium Intercalation into LiCoO<sub>2</sub>

The entropy of lithiation of Li<sub>x</sub>CoO<sub>2</sub> for 0.5 < x < 1.0 was also determined from measurements of the temperature-dependence of equilibrated voltages of electrochemical cells [79-81]. Measured changes in the entropy of the lithiation reaction were as large as 9.0 k<sub>B</sub>/atom, and as large as 4.2 k<sub>B</sub>/atom within the "O3" layered hexagonal structure of Li<sub>x</sub>CoO<sub>2</sub>. We performed a systematic study of the different contributions to the entropy of lithiation in Li<sub>x</sub>CoO<sub>2</sub>. The phonon entropy of lithiation was determined from measurements of inelastic neutron scattering. Time-of-flight scattering spectra were measured with the Pharos spectrometer at the Los Alamos National Lab., and were converted to approximate phonon densities-of-states (DOS), as shown on the right in Fig. 5(b). Phonon entropy accounts for much of the negative entropy of lithiation because the phonons in Li<sub>x</sub>CoO<sub>2</sub> have much higher frequen-

cies than those of Li metal [82]. On the other hand, the change of phonon entropy with lithium concentration was found to be small. Electronic structure calculations in the local density approximation gave a small electronic entropy of lithiation of the O3 phase.

The configurational entropy from lithium-vacancy disorder was large enough to account for most of the compositional trend in the entropy of lithiation of the O3 phase if there is a tendency for ordered structures to form at lithium concentrations of  $x=1/2$  and  $x=5/6$ . A consequence is that the two-phase region spans from  $0.83 < x < 0.95$ , somewhat stated in the literature [14,83].

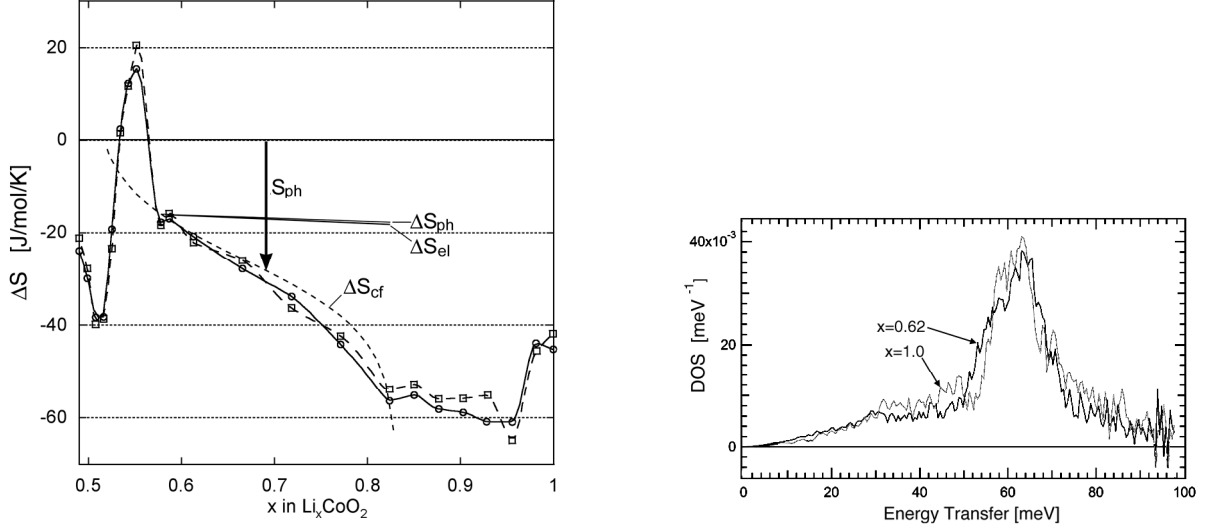


Figure 5. (a) Left: Configurational entropy  $\Delta S_{cf}$ , phonon entropy  $\Delta S_{ph}$ , and electronic entropy  $\Delta S_{el}$  contributions to the lithiation reaction in  $\text{Li}_x\text{CoO}_2$  over the composition range  $0.6 < x < 0.83$ , superimposed on the  $\Delta S$  measured from electrochemical data on OCV vs.  $T$ . The offset in the vertical arrow indicates the phonon entropy of intercalation  $S_{ph}$ , whereas  $\Delta S_{ph}$  is its change with  $x$  (neutron phonon DOS indicated approximately -20 J/mol/K). (b) Right: phonon DOS of  $\text{Li}_x\text{CoO}_2$ , for  $x=0.62$  and 1.0.

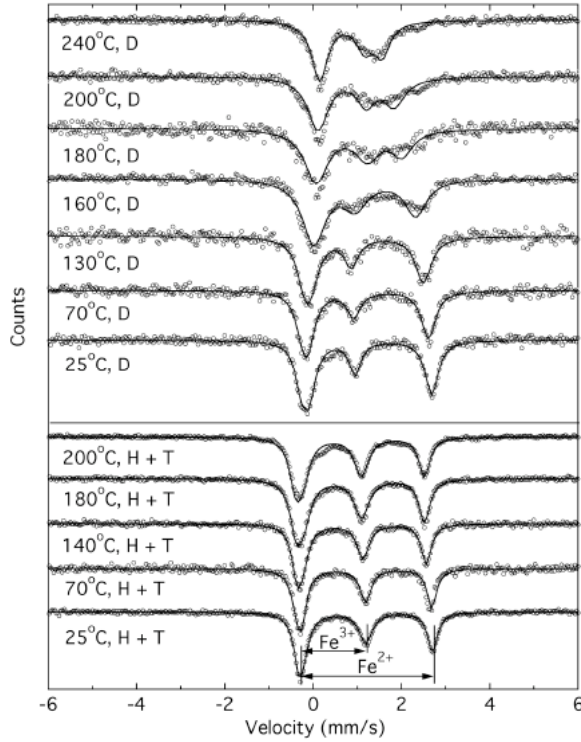
### 3 Dynamics of Transport in $\text{LiFePO}_4$

There is intense international interest in the olivine structure of  $\text{LiFePO}_4$  for service as a cathode material in rechargeable Li batteries. Compared to  $\text{LiCoO}_2$ ,  $\text{LiFePO}_4$  has reasonable electrochemical capacity, much lower cost, better safety characteristics, and better compatibility with the environment. Electrochemical insertion of  $\text{Li}^+$  into this material occurs by the transformation of heterosite ( $\text{FePO}_4$ ) into triphylite ( $\text{Li}_1\text{FePO}_4$ ). These two distinct phases have the same  $\text{FePO}_4$  framework, probably facilitating reversibility. The  $\text{Li}^+$  ions form one-dimensional chains in this framework, expanding it by 6.8% in volume.

The fundamental problem with  $\text{LiFePO}_4$  is poor electrical conductivity. Although the material is sufficiently conductive to be useful, it has many characteristics of an oxide insulator. Good success has been achieved by coating small particles of  $\text{LiFePO}_4$  with a conductive carbon, and practical electrodes are made with this approach [85-101]. Nevertheless, the rate capabilities are less than optimal, and the coating step requires careful process control.

#### 3.1 Valence Fluctuations of $^{57}\text{Fe}$ in Disordered $\text{Li}_{0.6}\text{FePO}_4$

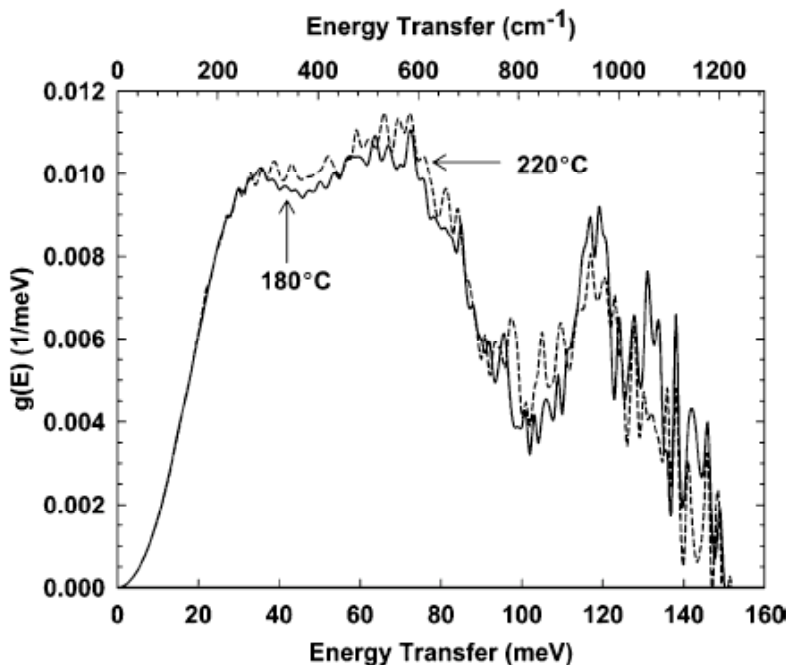
The local electronic structure around iron ions in  $\text{Li}_{0.6}\text{FePO}_4$  was studied by  $^{57}\text{Fe}$  Mössbauer spectrometry at temperatures from 25-240 °C. The equilibrium two-phase, triphylite plus heterosite, material was compared to a disordered solid solution that was obtained by quenching from a high temperature. Substantial electronic relaxations were found in the disordered solid solution compared to the two-phase material at temperatures of 130 °C and above. Fluctuations in the electric field gradient showed an approximately Arrhenius behavior, with an activation energy of  $335 \pm 25 \text{ meV}$ , and a prefactor of  $5 \times 10^{11} \text{ Hz}$ , while Arrhenius plots for the isomer shift showed activation energies of approximately 600 meV. It is suggested that these spectral relaxations are caused by the motions of  $\text{Li}^+$  ions. A slight relaxation at 180 °C in 10% of the two-phase material can be attributed to defects in the heterosite and triphylite phases. Overall, the disordered solid solution phase shows faster electronic dynamics than the two-phase material [102].



Mössbauer spectra of samples of  $\text{Li}_{0.6}\text{FePO}_4$  prepared as two-phase mixture (H+T) and disordered solid solutions (D) [102].

### 3.2 Phonons and Thermodynamics of Unmixed and Disordered $\text{Li}_{0.6}\text{FePO}_4$

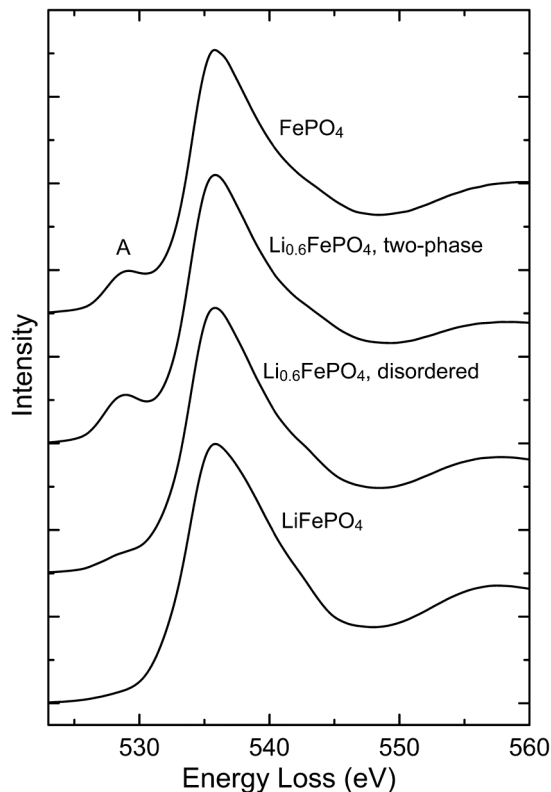
The lithium-storage material  $\text{Li}_{0.6}\text{FePO}_4$  was studied by inelastic neutron scattering and differential scanning calorimetry [103].  $\text{Li}_{0.6}\text{FePO}_4$  undergoes a transformation from a two-phase mixture (heterosite and triphylite) to a disordered solid-solution at 200 °C. Phonon densities of states (DOS) obtained from the inelastic neutron scattering were similar for the two-phase sample measured at 180 °C and the disordered sample measured at 220 °C. The vibrational entropy of transformation is 1.8 (0.9 J/(K mol)), which is smaller than the configurational entropy difference of approximately 3.1 J/(K mol). The measured enthalpy of the disordering transition was estimated as 2.5 kJ/mol. The phonon data show a small change in lattice dynamics upon disordering.



Experimental phonon DOS curves for  $\text{Li}_{0.6}\text{FePO}_4$  at 180 °C (solid) and 220 °C (dashed), normalized to unity [103].

### 3.3 Local Electronic Structure of Olivine Phases of $\text{Li}_x\text{FePO}_4$

Changes in the local electronic structure at atoms around Li sites in the olivine phase of  $\text{LiFePO}_4$  were studied during delithiation [104]. Electron energy loss spectrometry is used for measuring shifts and intensities of the near-edge structure at the  $K$ -edge of O, and at the  $L$ -edges of P and Fe. Electronic structure calculations are performed on these materials using a plane-wave pseudopotential code and an atomic multiplet code with crystal fields. It is found that both Fe and O atoms accommodate some of the charge around the  $\text{Li}^+$  ion, evidently in a hybridized Fe-O state. The O 2p-levels appear to be fully occupied at the composition  $\text{LiFePO}_4$ . With delithiation, however, these states are partially empty, somewhat suggestive of a more covalent bonding to the oxygen atom in  $\text{FePO}_4$  compared to  $\text{LiFePO}_4$ . The same behavior is found for the white lines at the Fe  $L_{2,3}$ -edges, which also undergo a shift in energy upon delithiation. A charge transfer of up to 0.48 electrons is found at the Fe atoms, as determined from white line intensity variations after delithiation, while the remaining charge is compensated by O atoms. No changes are evident at the P  $L_{2,3}$ -edges.



Oxygen *K*-edge from  $\text{Li}_x\text{FePO}_4$ . The spectra were normalized with a 40 eV window after the main peak.

### 3.4 Summary of Dynamics in Olivine Phases of $\text{Li}_x\text{FePO}_4$

The  $\text{Li}^+$  ions cause changes in the local electronic structure in their immediate neighborhood, evidently changing the occupancy of nearby Fe-O molecular orbitals [103]. These changes are seen in the EELS studies on Fe and O absorption edges, and can be quantified with the assistance of electronic structure calculations. At elevated temperatures, both the  $\text{Li}^+$  ions and the valence begin to move. This is most evident in the disordered solid solution phase of  $\text{LiFePO}_4$ , suggesting that this material has a higher intrinsic electronic and ionic conductivity. Interestingly, the  $\text{Li}^+$  hopping frequency can account for the full electrical conductivity. The polaronic conductivity is still expected to be the primary mechanism, however, so we propose that the motions of  $\text{Li}^+$  and polarons are coupled, at least in the disordered solid solution where these dynamics are fast. Stabilizing the disordered solid solution at operating temperatures of rechargeable batteries appears to be a promising approach to improving the intrinsic rate capabilities of  $\text{LiFePO}_4$ .

## 4 Research Team

The principal investigator for this work is Brent Fultz, Professor of Materials Science and Applied Physics at Caltech. He has supervised the completion of two Ph.D. theses during the past three years in the field of electrochemistry and materials. These were Dr. Jason Graetz, who is a postdoctoral fellow at Brookhaven National Lab., and Yvan Reynier, who received his Ph.D. in Materials Science from Grenoble University under the supervision of Rachid Yazami and co-supervision of B. Fultz. Dr. Reynier is now a postdoctoral fellow with CNRS, Grenoble. A postdoctoral fellow who worked on research under this grant, Dr. Heike Gabrisch, is now Assistant Prof. of Chemistry at the Univ. of New Orleans. Dr. Adrian Hightower, who received his Ph.D. from Caltech in 2000 in the previous budget period, has just been appointed Assistant Professor of Physics, Occidental College. Just before his untimely death in 2002, Dr. Charles Witham, who received his Ph.D. under this previous budget period, was promoted to technical staff member at the Jet Propulsion Laboratory.

Rachid Yazami, Director of Research at CNRS, Grenoble, has been a Visiting Associate in Materials Science at Caltech for five years. A cooperative agreement was reached between Caltech and the CNRS to establish a CNRS international Laboratory at Caltech on the subject of Materials for Electrochemical Energetics. This arrangement was terminated at the end of this DOE BES program. Dr. Channing Ahn at Caltech has collaborated with us for many years on TEM and EELS studies of materials, and has supervised graduate student thesis research in this area. Likewise, Prof. Peter Rez of Arizona State Univ. has interacted with us for over a decade on cross-section calculations of inelastic electron scattering, and has been working closely with us over the past 2 years.

Mr. Shu Miao has performed most of the EELS work reported in Section 2.2. He has finished his Ph.D. thesis research, filed his thesis, and has started a postdoctoral appointment in Toulouse, France. Ms. Joanna Dodd has completed her thesis, and will defend it on March 14, 2007. Mr. Yasunori Ozawa, who completed his thesis at Grenoble Univ., in 2006 while working at Caltech on materials modifications and capacity fade.



## 5 Bibliography

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